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Laboratory Evaluation of an Impinger Collection/Ion Chromatographic Source Test Method for Formaldehyde

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An impingr collection/ion chromatographic source test method for formaldehyde was developed and evaluated. An impinger solution of 3% hydrogen peroxide/0.025 N sodium hydroxide was used to oxidize known amounts of formaldehyde to formate ion, which is readily analyzed by ion chromatography. After standing overnight, samples were diluted 1:5 and then analyzed on a Dionex Model 14 ion chromatograph having a standard anion separator column, an anion suppressor column, and a conductimetric detector. Using 0.0025 M $Na_2B_4O_7$ as the eluent and mass transfer, by volatilization, of paraformaldehyde directly into collection impingers as the formaldehyde-atmosphere generation technique, recoveries of 85 to 90 percent were achieved.

Unlike colorimetric methods for formaldehyde, ion chromatography is not subject to interference from phenol, which is present with formaldehyde in many source emissions. In addition, interferent tests showed that the ion chromatographic method is not subject to interference from trioxane, a stable formaldehyde polymer, or from hexamethylene tetramine, a frequently used source of formaldehyde in industrial processes.

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LABORATORY EVALUATION OF AN IMPINGER COLLECTION/ ION CHROMATOGRAPHIC SOURCE TEST METHOD FOR FORMALDEHYDE

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessing environmental monitoring technology and systems; implementing Agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise, and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

This investigation was performed at the request of the Office of Air Quality Planning and Standards. A source test method was studied for the measurement of formaldehyde emissions from phenol-formaldehyde processes. Since phenols are interferents in many methods for analyzing formaldehyde, ion chromatography was selected because of its ability to resolve interfering materials. The work included studies of techniques for generating test atmospheres, procedures for converting formaldehyde to formate for ion chromatographic analysis, and the efficiency of components in the sample collection system. The present report deals with laboratory aspects of this investigation.

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ABSTRACT

This project was undertaken to evaluate and standardize a source test method for formaldehyde. Laboratory evaluation of a chromotropic acid method for measuring formaldehyde in the effluent of formaldehyde manufacturing plants was originally planned. However, a literature review indicated that this method is subject to interference from phenol, which is present with formaldehyde in many source emissions. Laboratory efforts were therefore concentrated on ion chromatographic analysis, which is not subject to phenol interference.

An impinger solution of 3% hydrogen peroxide/0.025 N sodium hydroxide was used to oxidize known amounts of formaldehyde to formate ion, which is readily analyzed by ion chromatography. After standing overnight, samples were diluted 1:5 and then analyzed on a Dionex Model 14 ion chromatograph having a standard anion separator column, an anion suppressor column, and a conductimetric detector. With 0.0025 M $Na_2B_4O_7$ as the eluent, the peroxide and formate peaks were well separated, eliminating any analysis problems resulting from alkaline hydrogen peroxide interference.

Mass transfer, by volatilization, of paraformaldehyde directly into collection impingers was found to be generally effective in generating known atmospheres of formaldehyde. However, there are problems inherent in this generation method, possibly due to the formation of products in addition to formaldehyde (i.e., water vapor, formic acid, and methyl formate). An alternative formaldehyde-generation method employing vapor-phase depolymerization of trioxane is recommended for further studies of the source test method.

Two compounds that potentially could be oxidized to formate were tested as possible interferents to the ion chromatographic method. S-trioxane was tested as an example of a stable formaldehyde polymer. Hexamethylene tetramine, a frequently used source of formaldehyde in industrial processes, was also tested. Only small formate peaks, possibly due to impurities, were observed for each compound, indicating little or no interference.

The impinger collection/ion chromatographic source test method was determined to be suitable for field applications. A field test at a plant with formaldehyde emissions is recommended to verify the source test method.

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SECTION 1

INTRODUCTION

Formaldehyde has been linked to eye and upper respiratory tract irritations, headaches, drowsiness, and gastrointestinal problems.[1] Formaldehyde may react with hydrochloric acid in humic air to form bis(chloromethyl)ether, a known carcinogen, and preliminary results released by the Chemical Industry Institute of Toxicology indicate that formaldehyde itself is a carcinogen in rats.[2] In anticipation of the regulation of formaldehyde by the Environmental Protection Agency's Office of Toxic Substances, this project was undertaken to evaluate and standardize a source test method for the chemical.

Laboratory evaluation of a chromotropic acid method for measuring formaldehyde in the effluent of formaldehyde manufacturing facilities was originally planned. However, the literature review conducted at the beginning of the project indicated that the chromotropic acid method is subject to interferences from phenol,[3] which is likely to be present with formaldehyde in many source emissions. Consequently, laboratory efforts were concentrated instead on ion chromatography, a relatively new analysis technique[4] that is not subject to phenol interference. Because formaldehyde can be oxidized in alkaline hydrogen peroxide solution to formate ion, which is readily analyzed by ion chromatography, this approach was selected for evaluation.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

A source test method for formaldehyde employing impinger collection and ion chromatographic analysis was determined to be suitable for field applications. However, owing to changes in priorities, this method was not completely validated but is sufficiently well developed to be validated easily in the future. Unlike colorimetric test methods for formaldehyde, this method is not subject to phenol interference. A field test at a plant with formaldehyde emissions is recommended to verify the test method.

The major problem in evaluating the test method was generating known atmospheres of formaldehyde. Although mass transfer of paraformaldehyde by volatilization directly into collection impingers yielded recoveries of 85 to 90 percent when conditions were carefully controlled, there are problems inherent in this generation method, possibly due to the formation of products in addition to formaldehyde (i.e., water vapor, formic acid, and methyl formate). An alternative generation method[5] employing vapor-phase depolymerization of trioxane is recommended for further studies of the source test.

SECTION 3

LITERATURE SURVEY

APPROACH

A computerized search of Chemical Abstracts for the period 1972 to 1981 was conducted on the sampling and analysis of formaldehyde in ambient and source atmospheres. In addition, the current literature was monitored throughout the project.

FINDINGS

Although several methods are available for the determination of aldehydes in ambient air, only a few such methods have been reported for formaldehyde in source emissions. The reported sampling techniques for formaldehyde include solid sorbents, bags, and impinger solutions. The analytical techniques include spectrophotometry, gas chromatography, infrared spectroscopy, ion chromatography, and chemical analysis methods.

Examples of spectroscopic methods are the colorimetric[6] and fluorometric[7] techniques and the more recently developed Fourier-transform infrared spectroscopic[8] and laser excitation techniques.[9 10] Among the other methods, gas chromatography and mass spectrometry in conjunction with gas chromatography have been used in the direct analysis of aldehydes and also in methods requiring a derivatization step prior to analysis.[11 12] A validated method published by the National Institute of Occupational Safety and Health (NIOSH) employs midget-bubbler collection followed by polarographic analysis.[13 14] Beasley et al.[15] used silica gel coated with 2,4-dinitrophenylhydrazine for collection, followed by solid-sorbent extraction with acetonitrile prior to hydrazone analysis by reverse-phase, high-pressure liquid chromatography.

The most widely used method for sampling and analyzing formaldehyde is the modified chromotropic acid method.[16] The pararosaniline method and the 3-methyl-2-benzothiazolone hydrochloride (MBTH) method are also commonly used. These three methods are based on colorimetric determination. The chromotropic acid and pararosaniline methods are specific for formaldehyde, whereas the MBTH method is used to analyze for total aldehydes. The literature on the chromotropic acid method and other colorimetric methods for formaldehyde indicated that these methods are subject to interferences, the most serious of which is phenol, which is emitted with formaldehyde from phenol-formaldehyde resin manufacturing processes. At an 8:1 excess, phenol results in a negative interference of 10 to 20 percent in the absorbance reading obtained with the chromotropic acid method.[3]

Ion chromatography, a relatively new analysis technique,[4] is not subject to phenol interference. The oxidation products of phenol--catechol, hydroquinone, pyrogallal, and quinone--do not interfere with ion chromatographic analysis for formate.

Kim et al.[17] developed a method for measuring formaldehyde in ambient air that is based on impregnated-charcoal collection and ion chromatographic analysis. Lorrain et al.[18] used ion chromatography in conjunction with two impinger sampling methods to analyze formaldehyde emissions from stationary sources. Recovery efficiencies of 94 and 100 percent were reported in the Lorrain study for formaldehyde levels of 100 ppm and 1 ppm, respectively.

RESULTS

Based on the literature survey, impinger collection followed by ion chromatographic analysis was selected for laboratory evaluation as a potential source test method for formaldehyde.

SECTION 4

EVALUATION PROCEDURES AND MATERIALS

Laboratory evaluation of the ion chromatographic method involved development of procedures specifically for analyzing formate ion in a matrix of alkaline hydrogen peroxide; generation of formaldehyde atmospheres of known concentration; development of sampling procedures; and testing of potential interferents.

ANALYSIS PROCEDURES

Ion exchange has long been a powerful tool for separating ions in solution. In the past, however, conductimetric detection was impractical with this method because of the large background produced by the electrolytic eluent used in the separation. The recently developed ion chromatographic technique greatly reduces the background, allowing a conductimetric detector to be used. The key to the technique is an eluent-suppressor column in series with the separator column. To separate anions, an anion exchanger is used in the separator column and a strong-acid cation exchanger in the H^+ form is used in the suppressor column. The eluent is suppressed before it reaches the detector, leaving a weakly conductive acid as the effluent. The sample ions are detected in their acid form.

Equipment

All analyses were performed on a Dionex Model 14 ion chromatograph equipped with a 3-mm × 500-mm standard anion separator column, a 6-mm × 250-mm anion suppressor column, and a conductimetric detector.

Kim et al. demonstrated that formate ion is easily analyzed by ion chromatography.[17] Under standard conditions (0.003 M $NaHCO_3$/0.0024 M Na_2CO_3 eluent at a rate of 138 mL/h; columns as described above), the retention time is approximately 3 min, but an interference results from the alkaline hydrogen peroxide used in converting formaldehyde to formate. However, with 0.0025 M $Na_2B_4O_7$ as the eluent, the peroxide and formate peaks are found to be well separated (Figure 1).

Calibration Standards

A 1,000-μg/mL stock formate standard was prepared by dissolving 1.5110 g sodium formate in 1 L deionized water. Calibration standards prepared by diluting the stock solution in alkaline hydrogen peroxide (0.6% H_2O_2/0.005 N NaOH) were linear over the range 10 to 100 μg/mL (Figure 2). At concentrations greater than 100 μg/mL, the detector response became nonlinear due to incomplete dissociation of the formic acid (a weak acid) formed in the

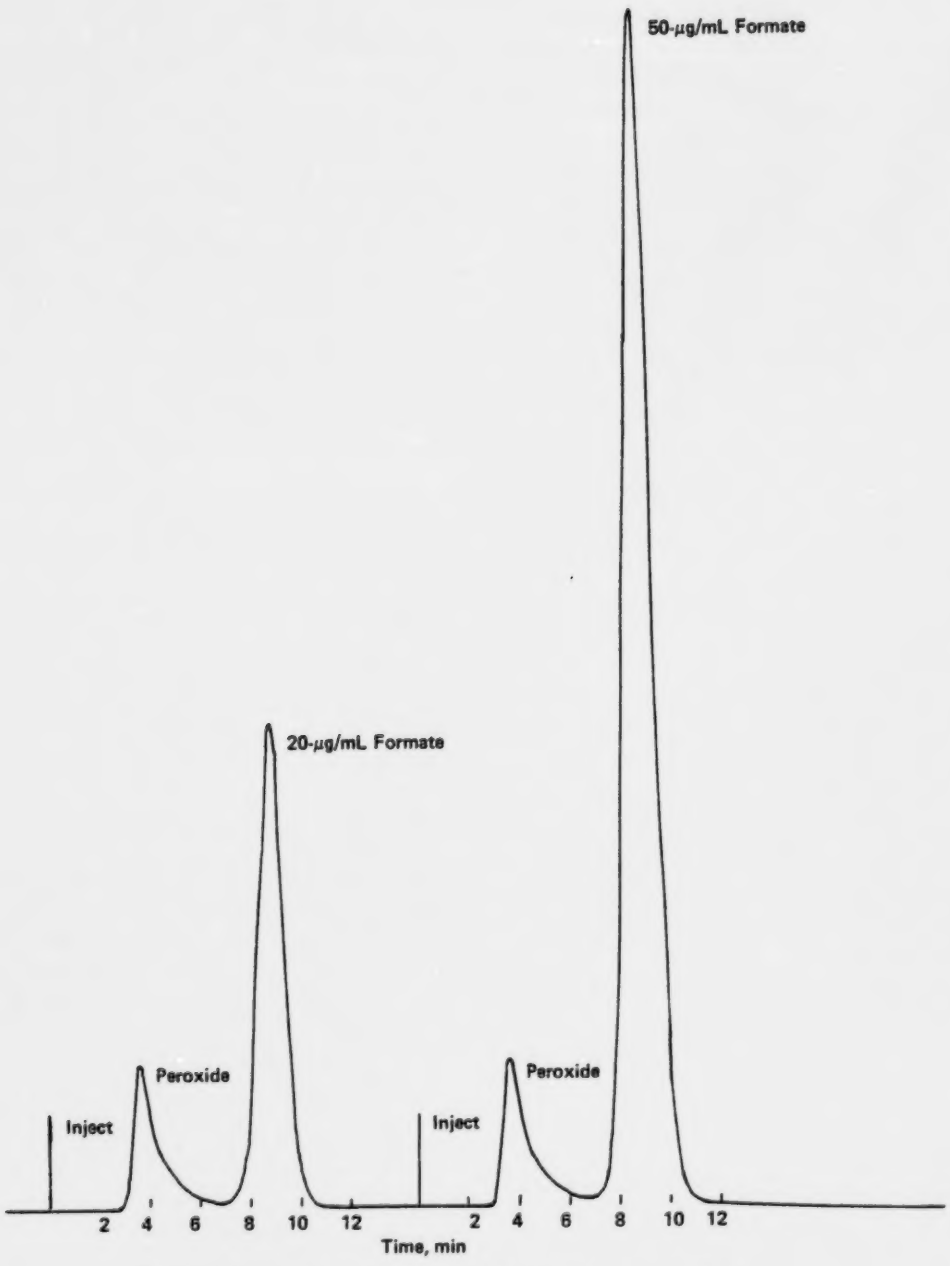

Figure 1. Separation of peroxide and formate peaks.

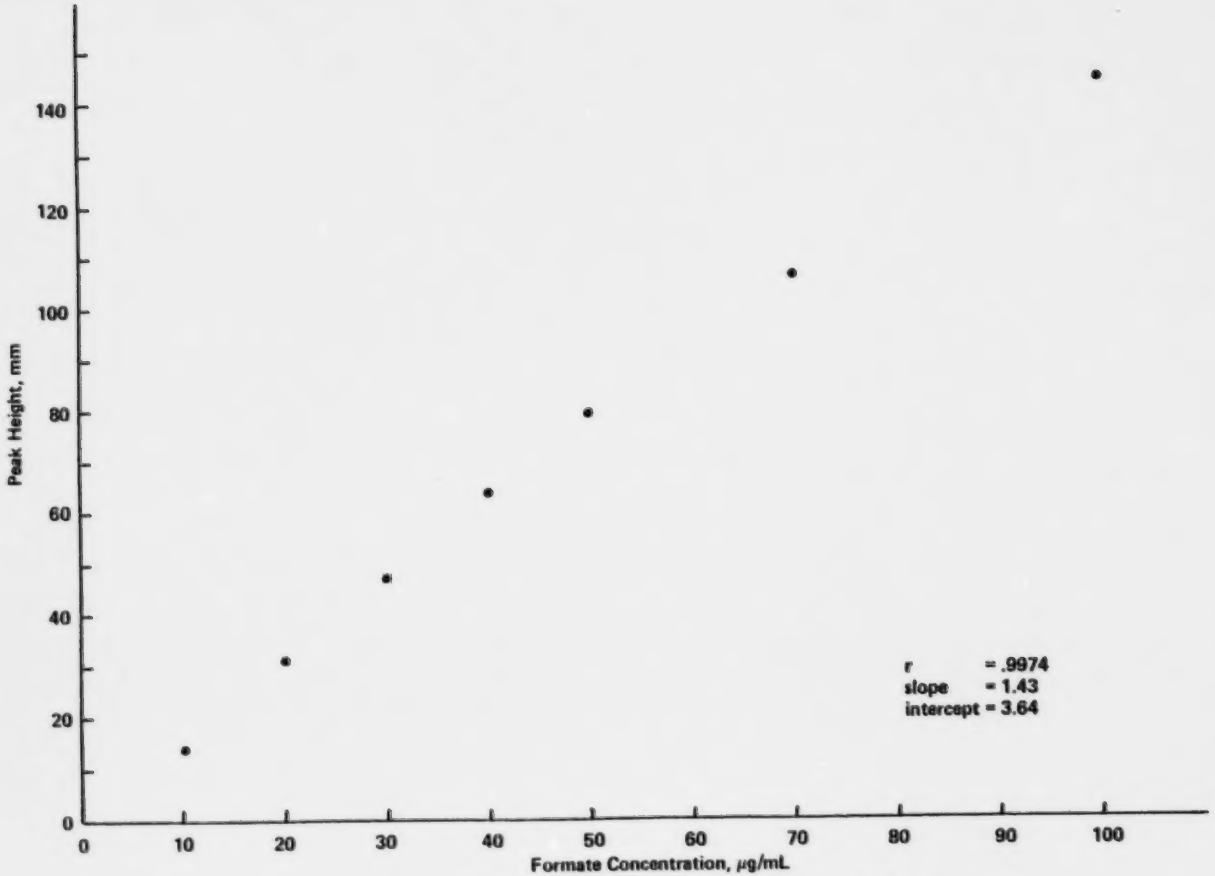

Figure 2. Calibration curve, 10- to 100-µg/mL formate.

suppressor column. For future research, dilution of samples of formate having concentrations greater than 100 μg/mL is recommended so that their concentrations will fall within the linear range.

Formate standards prepared in deionized water yielded sharper peaks and greater peak heights than those prepared in alkaline hydrogen peroxide. Therefore, all formate standards were prepared in the same concentration of alkaline hydrogen peroxide as the samples to be analyzed.

Calculations

Samples were analyzed for formaldehyde as formate. Formaldehyde is converted to formate according to the reaction

$$HCHO + H_2O_2 \rightarrow HCOO^-H^+ + H_2O \quad .$$

To calculate the concentration of formaldehyde in the original sample, the concentration of formate is multiplied by the ratio of the molecular weight of formaldehyde to the molecular weight of formate:

$$C_{HCHO} = C_{HCOO^-} \times \frac{MW_{HCHO}}{MW_{HCOO^-}}$$

$$= C_{HCOO^-} \times \frac{30.03}{45.02} \quad .$$

GENERATION OF FORMALDEHYDE ATMOSPHERES

A major problem in developing the source test method was generating atmospheres of known concentrations of formaldehyde for sampling. Of various generation methods reported in the literature,[5 18] three were evaluated: a permeation system, solid-phase depolymerization of paraformaldehyde into a Teflon bag (Teflon is a registered trademark of E. I. du Pont de Nemours & Co., Wilmington, DE), and solid-phase depolymerization of paraformaldehyde with direct collection into impingers.

Formaldehyde Permeation System

A Dynacal (a registered trademark of the Metronics Corp., Santa Clara, CA) formaldehyde-permeation device certified at 6,520 ng/min ± 2 percent at 100° C was placed in a glass tube inside an oven maintained at 100 ± 0.5° C. Zero air at 2 L/min was passed through approximately 6 m of copper tubing inside the oven before being passed through the permeation chamber. Samples

were collected at 1 L/min from a glass manifold, with the excess air being diverted to a hood.

Using the equation

$$C = \frac{(P)(Km)}{F}$$

where

C = concentration (ppmV)

P = permeation rate (ng/min)

K_m = molar constant (24.46/MW = 0.815 for formaldehyde)

F = flow rate over device (cc/min),

a concentration of 2.66 ppm or 3,261 $\mu g/m^3$ was obtained. Samples collected using this rate yielded inconsistent recoveries. To check the rate certified by the manufacturer, the permeation tube was weighed periodically over 2 months. The permeation rate was found to fluctuate, averaging approximately twice the rate certified by the manufacturer (see Table 1).

Solid-Phase Depolymerization of Paraformaldehyde into Teflon Bags

In an alternative generation method, an aluminum weighing boat containing a carefully weighed amount of solid paraformaldehyde was placed in a heated glass tube, zero air was passed through the tube at a carefully measured rate, and the resulting mixture was carefully confined in a Teflon bag (see Figure 3). This system initially resulted in low recoveries (30 to 70 percent), which were attributed to one or more of the following problems:

1. Loss of formaldehyde to the walls of the bag
2. Loss of formaldehyde to parts of the generation system prior to the bag
3. Formation of aerosol particles consisting of formaldehyde polymers
4. Nonstoichiometric decomposition of paraformaldehyde (i.e., formation of other compounds, such as water vapor, formic acid, and methyl formate).[19]

To improve the recoveries, a larger glass tube was used; the aluminum weighing boat was placed on an asbestos pad to ensure more even heating; the entire length of glass tube was wrapped in heating tape; the internal temperature was controlled at 180° to 190° C; and a glass-wool plug was placed in the end of the tube to trap particles. In addition, the Teflon bag was mildly heated with a heat gun during sample collection. As discussed in Section 5.0, these modifications yielded significant improvements.

TABLE 1. PERMEATION RATES FOR DYNACAL FORMALDEHYDE-PERMEATION DEVICE

Date	Time	Weight (g)	Δ Time (min)	Δ Weight (μg)	Permeation rate (ng/min)
5/8/81	14:22	12.353515			
			8,638	119,879	13,878
5/14/81	14:20	12.233636			
			21,728	297,486	13,691
5/29/81	16:28	11.936150			
			28,802	270,871	9,405
6/18/81	16:30	11.665279			
			5,715	62,315	10,904
6/22/81	15:45	11.602964			
			11,512	146,171	12,697
6/30/81	15:37	11.456793			

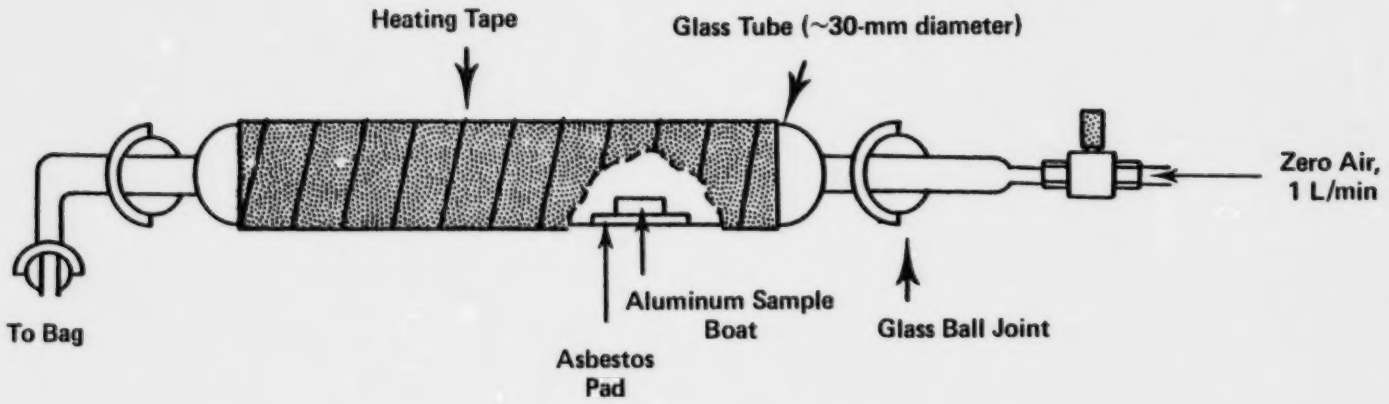

Figure 3. Formaldehyde-generation system for bag samples.

Solid-Phase Depolymerization of Paraformaldehyde with Direct Collection into Impingers

A third formaldehyde-generation method involves the mass transfer, by volatilization, of a known amount of paraformaldehyde from the heated glass tube directly into impingers containing the absorbing solution (Figure 4). Although this method does not generate a uniform formaldehyde atmosphere, the formaldehyde is in the gas phase when collected and losses to the walls of the bag are eliminated. Rapid volatilization resulted in low recoveries with this method, but recoveries of about 90 percent were achieved when volatilization was carefully controlled at a slow rate. The position of the aluminum boat in the heated tube had a dramatic effect on the volatilization rate, the temperature in the tube being lower near the incoming zero air.

SAMPLING PROCEDURES

Optimizing the absorbing solution was critical in developing a sampling method. Because hydrogen peroxide is an oxidizing agent in basic media but a reducing agent in acidic media, the pH of the absorbing solution had to be carefully controlled. Peroxide strength was also important; very low concentrations of peroxide may result in incomplete conversion, whereas high concentrations (6 to 9 percent) may result in oxidation of formate itself. A third important variable was the time required for complete conversion of formaldehyde to formate.

Absorbing Solution

Known samples prepared from 37 percent formaldehyde solution or sodium formaldehyde bisulfite in 3% hydrogen peroxide yielded pH's of 3.8 and, as expected, showed little or no conversion of formaldehyde to formate. Therefore, adjusting the pH by dropwise addition of sodium hydroxide until the solution was alkaline was necessary. Samples prepared in 3% hydrogen peroxide over the pH range 7.8 to 9.2 showed that conversion increased as the pH increased. The pH of 9.2 corresponds to an NaOH concentration of 0.025 N, the concentration recommended by Lorrain et al.[18] This concentration was selected for use.

Peroxide Concentration

Samples of 40 μg/mL formaldehyde were prepared at peroxide concentrations of 3, 6, and 9 percent. A plot of formate peak height vs. time at each concentration (Figure 5) shows that peak heights leveled off before conversion was complete at the higher peroxide concentrations. In fact, the formate peak height decreased after 24 h for the 9 percent peroxide sample, possibly due to decarboxylation. A peroxide concentration of 3 percent was selected for the absorbing solution.

Conversion-Time Studies

Spiked samples prepared in the 3% H_2O_2/0.025 N NaOH absorbing solution required 18 h for complete conversion, which agreed with the findings of

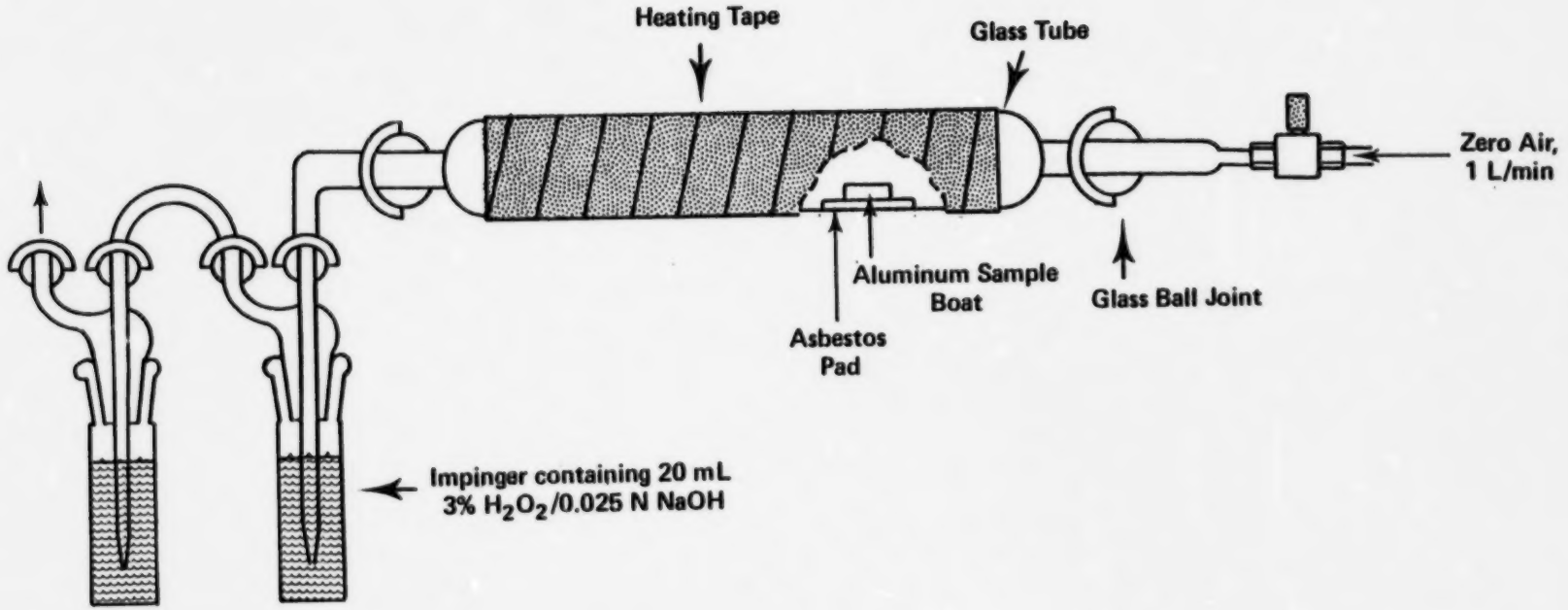

Figure 4. Formaldehyde-generation system: mass transfer.

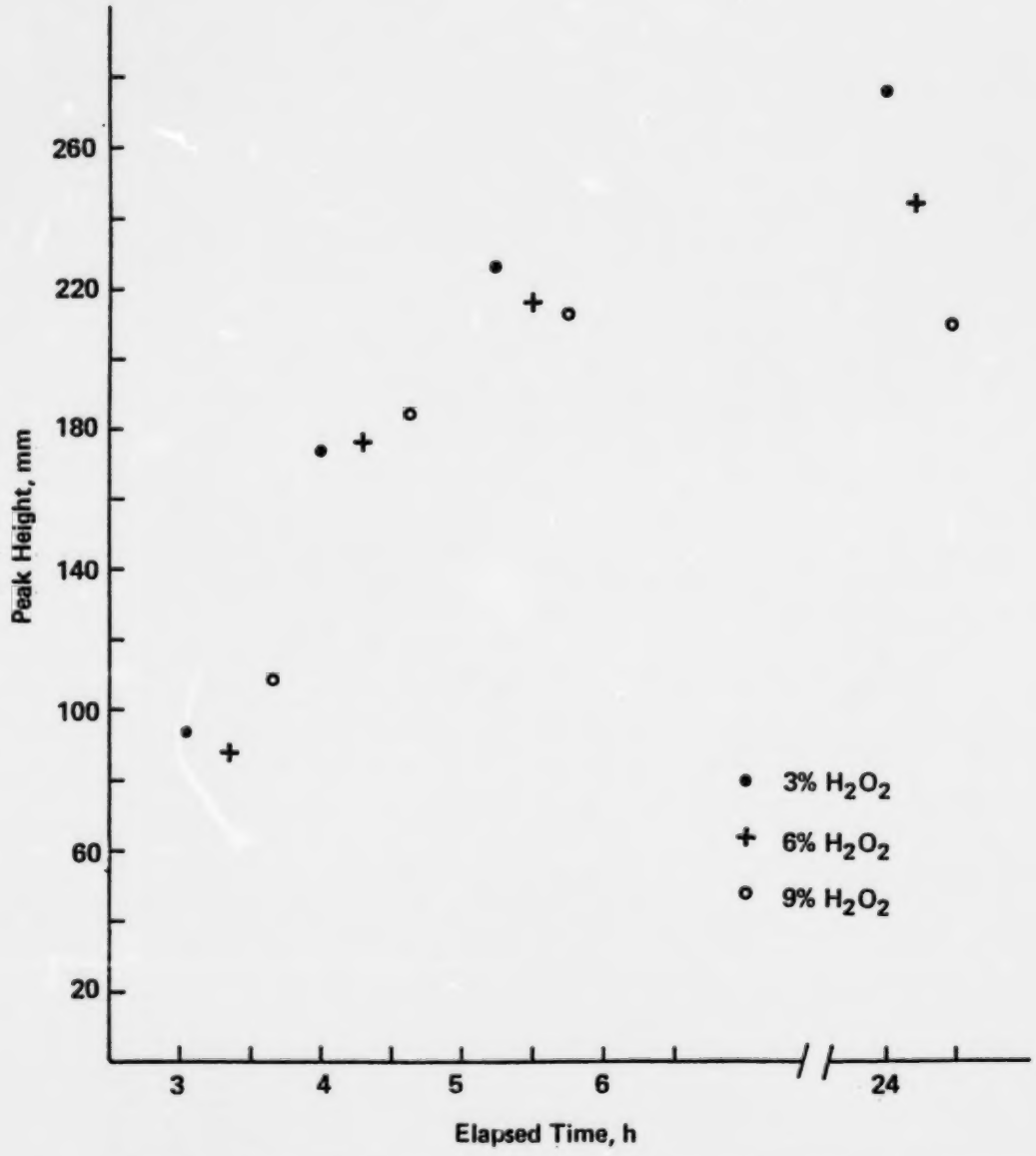

Figure 5. Effect of peroxide strength on conversion of formaldehyde to formate.

Lorrain et al.[18] To test the conversion of formaldehyde to formate using these optimized conditions, samples were prepared by adding known amounts of 1,000-μg/mL stock formaldehyde solution to volumetric flasks containing H_2O_2 and NaOH, so the final concentrations were 3% H_2O_2 and 0.025 N NaOH. After standing overnight, the samples were diluted 1:5 prior to ion chromatographic analysis (final concentrations were 0.6% H_2O_2 and 0.005 N NaOH). Formate calibration standards were prepared by diluting the formate stock solution, as discussed above. Table 2 summarizes the conversion efficiencies.

To reduce the time for conversion of formaldehyde to formate, the impinger solutions from several sample runs were heated at 60° C for 15 min, as described in Buchi.[19] This method, however, gave low and variable recoveries (45 to 80 percent) even when the samples were heated for 4 h at 60° C. Possible explanations are destruction of the peroxide before conversion was complete, or decarboxylation. Thereafter, samples were allowed to stand for 18 h for complete conversion.

Final Procedure

Several sampling runs were conducted using each of the formaldehyde-generation techniques discussed previously. Samples were collected at 1 L/min using two midget impingers in series, each containing 20 mL of 3% H_2O_2/0.025 N NaOH. After standing overnight, the samples were diluted 1:5 and analyzed by ion chromatography. The impingers initially were analyzed separately to check for breakthrough. Only a trace of formate, which was not easily quantifiable, was found in the sample of the second impinger. Therefore, formaldehyde vapor was judged to be collected completely by the first impinger; for subsequent samples, the two impingers were combined in a 50-mL volume and diluted 1:5 (final concentrations were 0.6 H_2O_2/0.005 N NaOH).

INTERFERENT TESTS

Two compounds that potentially could be oxidized to formate were tested as possible interferents to the ion chromatographic method. S-trioxane ($C_3H_6O_3$) was tested as an example of a stable formaldehyde polymer. Hexamethylene tetramine, or HMT ($C_6H_{12}N_4$), a frequently used source of formaldehyde in industrial processes, was also tested.

Procedures

A 1,000-μg/mL stock solution of each compound was prepared by dissolving 0.1 g in 100 mL deionized water. Samples of 20, 50, 100 μg/mL were prepared by diluting the stock solutions in 3% H_2O_2/0.025 N NaOH. After standing overnight, the samples were diluted 1:5 before analysis on the ion chromatograph.

TABLE 2. CONVERSION EFFICIENCY OF ABSORBING SOLUTION

CH_2O (μg/mL)	$CHOO^-$ theoretical, 1:5 dilution (μg/mL)	$CHOO^-$ found (μg/mL)	Percent conversion
100	30	28.8	96
150	45	45.2	100
200	60	58.4	97
250	75	72.6	97

SECTION 5

EVALUATION RESULTS AND DISCUSSION

ANALYSIS RESULTS

Teflon Bag Samples

Samples collected in Teflon bags initially produced good recoveries (93 percent or greater). As sampling continued, however, recoveries dropped to 50 to 70 percent (Table 3). Recoveries improved when the system was modified as discussed, but occasional low recoveries prompted the use of a different generation method. Bag samples collected after the system was modified were sampled completely to ensure that all formaldehyde was removed.

A standard deviation was calculated from the paired values of samples 1 and 4 through 7 (sample 2 was not included because equal gas volumes were not sampled; sample 3 was rejected as an outlier). The data were assumed to be homoscedastic and the deviations to be normally distributed. The standard deviation, 210 μg, indicates that relative precisions ranged from 6 to 14 percent.

Mass Transfer Samples

Samples collected through mass transfer, by volatilization, of paraformaldehyde from the heated glass tube directly into the impingers initially showed good recoveries (~90 percent), followed by an unexplained drop. When the generation system was modified as discussed, recoveries improved significantly, with only occasional low recoveries. A possible explanation for the low recoveries is incomplete volatilization of paraformaldehyde; minute amounts of solid paraformaldehyde remaining in the aluminum boat were observed to boil off rapidly due to superheating of the tube when the air supply to the tube was disconnected. Consequently, samples were thereafter collected until no trace of paraformaldehyde in the boat was visible. For the 45 sampling runs conducted with this modified system, recoveries ranged from 36 to 136 percent. The mean recovery was 84.3 percent, with a standard deviation of 21.4 percent. Possible explanations for the low recoveries were discussed above. Possible explanations for recoveries higher than 100 percent are errors in weighing or in standards preparation. All mass transfer data are presented in Appendix A.

Once conditions for generation, sampling, and analysis were optimized, a final series of runs was conducted. Control samples were prepared by dissolving known quantities of paraformaldehyde in the impinger solution. These samples yielded recoveries of 93 to 104 percent, with a mean of 98 percent. Samples collected using the mass transfer system were observed

TABLE 3. ANALYSIS RESULTS FOR TEFLON BAG SAMPLES

	CH_2O (mg)	V_{bag} (m^3)	Conc (mg/m^3)	V_{sample}, (m^3)	CH_2O theoretical (μg)	CH_2O found (μg)	Percent recovery
1	12.2	0.090	136.0	0.030	4,079	3,791	92.9
				0.030	4,079	3,888	95.3
2	11.6	0.080	144.6	0.046	6,579	7,313	111.1
				0.015	2,191	1,592	72.7
3	15.0	0.118	127.1	0.032	4,000	2,300	57.5
				0.032	4,000	1,000	25.0
4	23.336	0.124	188.4	0.032	6,027	3,017	50.0
				0.032	6,027	3,233	53.6
5	17.119	0.118	145.5	0.031	4,487	2,971	66.2
				0.031	4,487	3,171	70.6
6	18.574	0.148	125.8	0.031	3,886	1,796	46.2
				0.031	3,886	1,351	34.7
7	18.425	0.122	150.5	0.030	4,516	2,084	46.1
				0.030	4,516	2,521	55.8
			(Modifications to Generation System Made)				
8	4.872				4,872	4,413	90.6
9	0.571				571	343	60.0
10	0.413				413	256	62.0
11	0.159				159	170	106.9
12	0.991				991	805	81.2

carefully to ensure that the paraformaldehyde had been volatilized completely. When volatilization was controlled at a slow rate, recoveries ranged from 76 to 94 percent. The mean recovery for nine samples was 86.5 percent, with a standard deviation of 5.1 percent. The data are summarized in Table 4.

Linear regression analysis was performed on the data in Table 4 to determine if the percent recovery was level-dependent. One point--3,264 μg, 75.8 percent--was eliminated as an outlier. The variation of percent recovery with quantity of formaldehyde vaporized, 0.011 ± 0.003 percent/μg CH_2O, was small but significant at the 99 percent confidence level. Sampling precision, also obtained from the regression analysis, ranged from 7 percent for the smallest quantity of CH_2O vaporized to 5 percent for the highest quantity. Thus, there is evidence that recovery may become less efficient at lower CH_2O concentrations. On the other hand, the control samples gave excellent conversions and recoveries so that the CH_2O generation process may have been the real problem.

Geisling et al.[5] experienced similar inconsistencies in generating formaldehyde from paraformaldehyde and found that other compounds are released when this method is used. Consequently, they developed a generation system using vapor-phase depolymerization of trioxane, with reported conversions to formaldehyde of essentially 100 percent. This method is recommended for testing in any future research involving formaldehyde generation.

Interferent Tests

Only small formate peaks, possibly due to impurities, were observed for trioxane (Table 5) and HMT (Table 6), indicating little or no interference from these compounds.

TABLE 4. ANALYSIS RESULTS FOR MASS TRANSFER SAMPLES

CH_2O weighed (μg)	CH_2O recovered (μg)	Percent recovery	Comments
3,441	3,413	99.2	Control sample; no generation
3,104	3,063	98.7	Control sample; no generation
2,720	2,520	92.6	Control sample; no generation
2,831	2,651	93.6	
3,091	2,781	90.0	
2,328	1,997	85.8	
2,532	2,456	97.0	Control sample; no generation
2,532	2,162	85.4	
2,670	2,381	89.2	
1,417	1,009	71.2	Paraformaldehyde volatilized rapidly
2,212	2,018	91.2	
1,921	1,574	81.9	
2,500	2,179	87.2	
3,264	2,473	75.8	
2,768	2,889	104.3	Control sample; no generation
2,465	2,098	85.1	

TABLE 5. RESULTS OF TRIOXANE INTERFERENCE STUDIES

Trioxane undiluted sample (μg/mL)	Trioxane diluted 1:5 (μg/mL)	$CHOO^-$ observed (μg/mL)	CH_2O (μg/mL)
20	4	0.04	0.03
50	10	0.06	0.04
100	20	0.07	0.05

TABLE 6. RESULTS OF HEXAMETHYLENE TETRAMINE INTERFERENCE STUDIES

HMT, undiluted sample (μg/mL)	HMT diluted 1:5 (μg/mL)	$CHOO^-$ observed (μg/mL)	CH_2O (μg/mL)
20	4	0.06	0.04
50	10	0.06	0.04
100	20	0.07	0.05

SECTION 6

QUALITY CONTROL/ASSURANCE

PROCEDURES

Good laboratory practices were followed throughout the program. New reagent-grade chemicals were purchased and used only for this project. All glassware was carefully cleaned and checked for contamination. Ion chromatography standards as well as a calibration curve were prepared each day that samples were run. Blanks and spiked samples were run with the collected samples. All work was documented in a bound laboratory notebook.

Dr. William F. Gutknecht served as the Quality Control Officer for this project. Dr. Gutknecht periodically observed the laboratory experiments, reviewed notebooks, and provided advice on quality control.

CONTROL SAMPLES

There are no known formaldehyde reference samples. As discussed previously, control samples were prepared in-house to check conversion efficiencies by introducing known amounts of formaldehyde solution, sodium formaldehyde bisulfite, or paraformaldehyde directly into the impinger solutions.

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APPENDIX A
ANALYSIS RESULTS FOR MASS TRANSFER SAMPLES

CH_2O weighed (μg)	CH_2O recovered (μg)	Percent recovery
15,389	13,633	88.5
14,246	13,117	92.1
10,209	8,488	83.1
9,590	8,367	87.2
7,369	3,511	47.6
6,799	3,386	49.8
9,240	7,644	82.7
7,540	6,549	86.9
41,839	14,937	35.7
104,610	16,528	15.8
25,150	16,977	67.5
56,875	17,966	31.6
56,670	16,615	29.3
63,045	13,923	22.1
40,130	6,112	15.2
23,990	5,006	20.9
68,115	7,880	11.6
11,725	9,284	79.1
22,275	5,892	26.5
	(Modifications to Generation System Made)	
15,060	14,475	96.1
6,675	4,327	64.8
10,715	9,585	89.5
9,240	6,495	70.3
13,490	14,367	106.5
12,485	13,961	111.8
8,395	8,397	100.0
8,605	8,582	99.7

APPENDIX A (continued)

CH_2O weighed (μg)	CH_2O recovered (μg)	Percent recovery
8,240	8,225	99.8
18,560	17,641	95.0
17,790	15,314	86.0
29,655	21,797	73.5
8,035	8,057	100.3
20,345	7,887	38.8
34,150	15,345	44.9
7,785	7,280	93.5
7,785	7,677	98.6
8,650	8,591	99.3
12,045	11,055	91.8
7,520	7,747	103.0
3,060	2,581	84.3
1,280	977	76.4
3,380	1,212	35.9
1,120	791	70.6
2,110	2,868	135.9
2,614	3,192	122.1
2,000	2,342	117.1
2,520	2,517	99.9
2,325	2,323	99.9
235	236	100.4
331	333	100.7
308	215	69.7
284	215	75.6
204	143	70.3
1,900	1,583	83.3
226	170	75.2
346	240	69.3
2,638	2,257	85.5

APPENDIX A (continued)

CH_2O weighed (μg)	CH_2O recovered (μg)	Percent recovery
63	37	58.2
4,170	2,799	67.1
4,503	3,365	74.7
2,798	1,897	67.8
2,778	2,050	74.1
3,775	2,569	68.1
614	305	49.7
2,524	2,474	98.0 (Control sample, no generation)
2,334	2,255	96.6 (Control sample, no generation)